

LIQUID PHASE METHANATION OF HIGH CONCENTRATION CO SYNTHESIS GAS

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I INTRODUCTION

Development work on the Liquid Phase Methanation process commenced on April 25, 1972 and was first reviewed in October, 1972 at the 4th Annual Pipeline Gas Symposium. The development has proceeded in a very successful manner. Prior to reviewing these recent accomplishments, the basic Process and Program background will be briefly reviewed for those attendees who are not familiar with the technology.

A. Process Background

The Liquid Phase Methanation Process is ideally suited to the safe and reliable conversion of high concentration carbon monoxide streams to methane. The exothermic heat of reaction, which under adiabatic conditions could theoretically cause temperature rises of about 1700°F in a non-recycle situation is easily removed by the inert fluidizing liquid in a near isothermal system. This is achievable by effecting the heterogeneously catalyzed reaction of the feed gases in the presence of an inert liquid phase which absorbs the large exothermic heat of reaction. The reaction proceeds to near completion in a single pass and economic studies will dictate whether a single stage reactor will be used or if a polishing reactor should be utilized in the final design.

Figure 1 illustrates the process in more detail. The inert liquid is pumped upflow through the reactor at a velocity sufficient to both fluidize the catalyst and remove the reaction heat. The low BTU feed gas is passed cocurrently up the reactor where it is catalytically converted to a high concentration methane stream. The exothermic reaction heat is taken up by the liquid mainly as sensible heat and partly by vaporization (depending upon the volatility of the liquid). The overhead product gases are condensed to remove the product water and to recover any vaporized liquid for recycle. The main liquid flow is circulated through a heat exchanger where the heat of reaction is removed by generating high pressure steam. This also provides excellent temperature control for the system.

B. Project Background

Development of the Liquid Phase Methanation Process is included within the AGA/OCR joint program on synthetic natural gas production from coal. The development program is divided into three phases which have been proceeding in an overlapping manner. These are reviewed below:

<u>Phase</u>	<u>Object</u>	<u>Percent Completion</u>
I	Exploratory Research and Development	100
II	Construction and Operation of a Larger Scale Process Development Unit (PDU)	90
III	Construction and Operation of a Full Scale Integrated Pilot Plant	40

Completion of the program is scheduled for June 30, 1975.

II DESCRIPTION OF EQUIPMENT

A. Bench Scale

The bench scale reactor is 0.81" I.D. x 48" long. The nominal feed gas rate for this unit is 30 SCFH, and is supplied from premixed high pressure gas cylinders. Except for reaction temperature, the bench scale unit is substantially manually operated and controlled. The catalysts used in these studies were standard commercial methanation catalysts, ground to a 16-20 mesh size, which is compatible with the small reactor diameter.

B. Process Development Unit (PDU)

The nominal feed gas rate for the unit is 1500 SCFH which is a scale-up of 50-100 times the bench scale unit. The methanation reactor is 4" O.D. x 84" high and the catalyst bed height can be varied from 2 to 7 feet. The basic design and flow scheme of the PDU is similar to the bench scale unit. The product gases, following analysis, are sent to an incinerator where they are thermally oxidized to carbon dioxide and water prior to discharge to the atmosphere. Sufficient instrumentation is provided for complete automatic control and monitoring from a remote control room. The reactor is fitted with movable gamma ray detector which is used to measure density differences between the source (radioactive material) and the detector. In this manner we are able to accurately determine the height of the fluidized catalyst bed under varying reaction conditions.

The overall objectives of this phase of the program are:

- Determine effect of all process variables for optimum performance.
- Determine data needed for reliable engineering design and cost estimates of larger plants.
- Determine catalyst life, recovery and regeneration methods.
- Determine liquid life and effectiveness.
- Determine whether reaction model correlation is valid for PDU performance.

C. Pilot Plant

The third phase of the liquid phase methanation project is the design, construction and operation of a large pilot plant. The basic objectives are to demonstrate the process on a synthesis gas actually produced in a coal gasification process and obtain the necessary design and performance data such that detailed design and engineering can be accomplished for a full size (ca. 250 MM SCFD) coal gasification plant. The reactor design in the pilot plant is 2' diameter by 15' long. This we feel is large enough to provide adequate scale-up information for commercial sized reactors. Again, the design is basically the same as for the PDU and bench scale unit, but obviously modified and adapted for the larger capacity. The scheduled start-up of the pilot plant is June, 1975.

The pilot plant will be located at the site of an existing coal gasification process. At this time, the two most logical places are the IGT plant in Chicago or the CO₂ Acceptor plant in Rapid City, South Dakota. The design concept is to build a skid-mounted unit that could be located at either place or at other locations where coal gasification processes are under construction. With a skid-mounted unit, it could be operated at one site for a period of time and then moved to another location for testing with synthesis gas from another coal gasification process.

The design of the unit is such that it can accommodate synthesis gas feed from any one of a number of processes. The unit will be designed to handle a maximum feed gas of 2 MM SCFD at 1100 psig. This is the maximum output of the IGT Hygas plant. The LPM process can also operate at lower pressure and, hence, Rapid City would handle the lower pressure feed gas. The synthesis gas feed there is only 0.6 MM SCFD and is available at 100 psig.

III REACTION CORRELATING MODEL

One of the goals of our experimental program in the bench scale unit was to develop the necessary correlations for use in the ultimate design of large commercial plants. With the complexity inherent in the three phase, gas-liquid-solid reaction systems, many models can be postulated. As a background to how a reaction model was finally selected, the physical situation in the three phase system is briefly reviewed.

1. The gas bubbles, after entering the reactor, rise due to convection and buoyancy. On the other hand, the presence of a solid phase retards the upward bubble motion according to its void spacing and particle size.
2. The reactants are transferred from the gas bubbles to the bulk liquid through the gas-liquid interface. Consideration of the relative resistances shows that the liquid film coefficient at the gas-liquid interface should be the least efficient mass transfer step and that the liquid phase concentration at the gas-liquid interface is governed by Henry's Law.
3. The reactants, after diffusing from the gas-liquid interface to the bulk liquid, are convected by the fluid motion to the liquid-catalyst interface.
4. Mass transfer of the reactants from the bulk liquid across the liquid catalyst interface should again be governed by the liquid film coefficient.
5. After absorbing on the catalyst surface, the reactants undergo a catalytic surface reaction.
6. The reaction products desorb and are transferred back to the gas bubbles according to Steps 4 to 1.

As our first approach to the model we considered the controlling step to be one of the following:

- The mass transfer from gas to liquid.
- The mass transfer from liquid to catalyst.
- The catalytic surface reaction step.

The other steps were eliminated since convective transport with small catalyst particles and high local mixing should offer virtually no resistance to the overall reaction scheme. Mathematical models were constructed for each of these three steps.

Our initial experimental results indicated that the kinetic model — first order in liquid phase CO concentration — was the leading candidate. We designed an experimental program then with this reaction model specifically in mind. The integrated rate expression (1) can be written as:

(1) See Appendix for nomenclature.

$$\ln \left(\frac{1}{1-X_T} \right) = \frac{k(P_T - P^*)}{K_{H_{CO}} (M/p_L) (1-2Y_{CO}^0) F^0} W$$

Therefore a plot of:

$$\ln \left(\frac{1}{1-X_T} \right) \quad \text{as} \quad \frac{(P_T - P^*)}{F^0 (1-2Y_{CO}^0)} W$$

should result in a straight line through the origin, where the slope $k/K_H (M/p_L)$ is a direct measure of the catalyst-liquid pair productivity.

Bench Scale Results

We performed this type of process variable scan for several sets of catalyst-liquid pairs. A representative example is shown in Figure 2. In all cases, the data supported the proposed mechanism. In addition, we examined the effect of temperature on the kinetic rate constant, and a typical Arrhenius plot is shown in Figure 3. The activation energy calculated for all of the systems run in the bench scale unit fell within 18,000 to 24,000 cal/gm mole.

Data collected (see Figure 4) during these process variable scans indicated that a larger than expected amount of CO_2 was also being formed. Selectivity to CO_2 reached a maximum of 5-10% at about 90-95% CO conversion. At higher conversions, the CO_2 level is reduced either by reverse shift and subsequent methanation of CO , or by direct methanation of CO_2 . This selectivity to CO_2 can be eliminated by cofeeding small amounts of CO_2 (3-5%). Since multiple CO_2 absorbers are required in the commercial SNG plant, one or more could be relocated downstream of the methanation step. This could offer some economic advantages since CO_2 absorption would now occur at higher concentration and pressure and lower total gas flow.

Process Development Unit Results

Work in the PDU largely paralleled the bench scale reactor tests, with one important addition - extensive three-phase fluidization studies. As we have previously mentioned, the PDU is equipped with a traversing gamma ray density detector, capable of measuring the bed density within ± 0.01 specific gravity units. In this manner we were not only able to measure and correlate fluidized bed expansion as a function of liquid and gas velocities and physical properties but we were also able to determine the individual phase volume fractions. The two major findings of this work were (see Figure 5); (1) the absolute values for the gas holdup are 3-4 times greater than the incremental porosity increase due to the gas flow at constant liquid flow, and (2) the gas holdup is essentially independent of liquid velocity for $1.3 U_{mf} < U_L < 2.5 U_{mf}$. In addition, the data for all the catalysts indicated that the maximum gas volume fraction obtainable was on the order of 0.5-0.6.

Reaction studies were carried out in the PDU in order to verify the correlating model developed in the bench scale unit. This provides data applicable to the scale-up design required for the pilot plant, and ultimately, the commercial unit. The initial work in the PDU was performed with particles much larger ($1/8"-3/16"$) than those used in the bench scale unit ($< 1/32"$), and the reaction rates for

these larger particles were about one-third the rates obtained with the smaller size particles (compare Figures 2 and 6). In addition, the activation energy obtained with this data was on the order of 11,000 cal/gm mole; just about one-half the value obtained in the bench unit (compare Figures 3 and 7). These results suggested that we were encountering pore diffusion limitations, and we attempted to verify this result by investigating still smaller particles (1/16"). While the reaction rates increased significantly, as they should, the activation energy remained essentially unchanged, indicating that we were still in the pore diffusion regime. Therefore, we can still further increase productivity by simply reducing particle size. This should not be too difficult since 1/32" particles are already being used in analogous commercial systems. The ultimate productivity obtainable has not yet been accurately defined, although we are confident that a vapor hourly space velocity of 4000 hr⁻¹ at 1000 psig and 650°F with a feed containing 20% CO, 60% H₂, and 20% CH₄ should result in a CO conversion of 95-98%. One should bear in mind that these results do in fact confirm the first order reaction rate model proposed as a result of the earlier bench scale results. Future work will concentrate on the effect of axial dispersion arising from the varying geometries encountered during scale-up and on determining the optimum particle size for the commercial unit.

In an attempt to define useful catalyst life, we have conducted continuous runs of 2 and 4 weeks duration. These results have been encouraging in that after an initial period of deactivation over the first 50-100 hours (common with nickel hydrogenation catalysts), the catalyst reaches an equilibrium productivity in excess of our original design basis of a VHSV equal to 4000 hr⁻¹ at 1000 psig and 650°F. Considering these results, and our substantial experience with all types of catalysts, we have every reason to believe that a catalyst life in excess of one year can be achieved at which point catalyst replacement costs are insignificant on overall SNG economics.

IV CONCLUSIONS

Based on this past work and ongoing experiments, we feel that the Liquid Phase Methanation process promises to become an economic, reliable and versatile means of converting synthesis gas mixtures to high BTU gas. Chem Systems believes this technology to be a key step in the transformation of fossil feeds to pipeline gas and we look forward to its successful application in commercial coal gasification plants.

e_G	= Gas Phase Volume Fraction
e_L	= Bed Porosity; Liquid Only Fluidizing
e_{LG}	= Bed Porosity; Liquid and Gas Fluidizing
F	= Gas Flow Rate at any Position; g moles/sec
k	= Reaction Rate Constant; g moles/sec-gm catalyst-(g mole/cm ³)
K_H	= Henry's Law Coefficient; atm/mole fraction
M	= Liquid Phase Molecular Weight; gm/g mole
ρ_L	= Liquid Phase Density; gm/cm ³
P_T	= Total Pressure; atm
P^*	= Liquid Phase Vapor Pressure; atm
T	= Temperature, °K
U_{mf}	= Minimum Fluidization Velocity; cm/sec
U_{OG}	= Superficial Gas Velocity at Reactor T and P_T ; cm/sec
W	= Weight of Catalyst; gms
X_T	= Fraction of CO Converted

Super Script

0 = Initial Condition

FIGURE 1

LIQUID PHASE METHANATION PROCESS SCHEMATIC

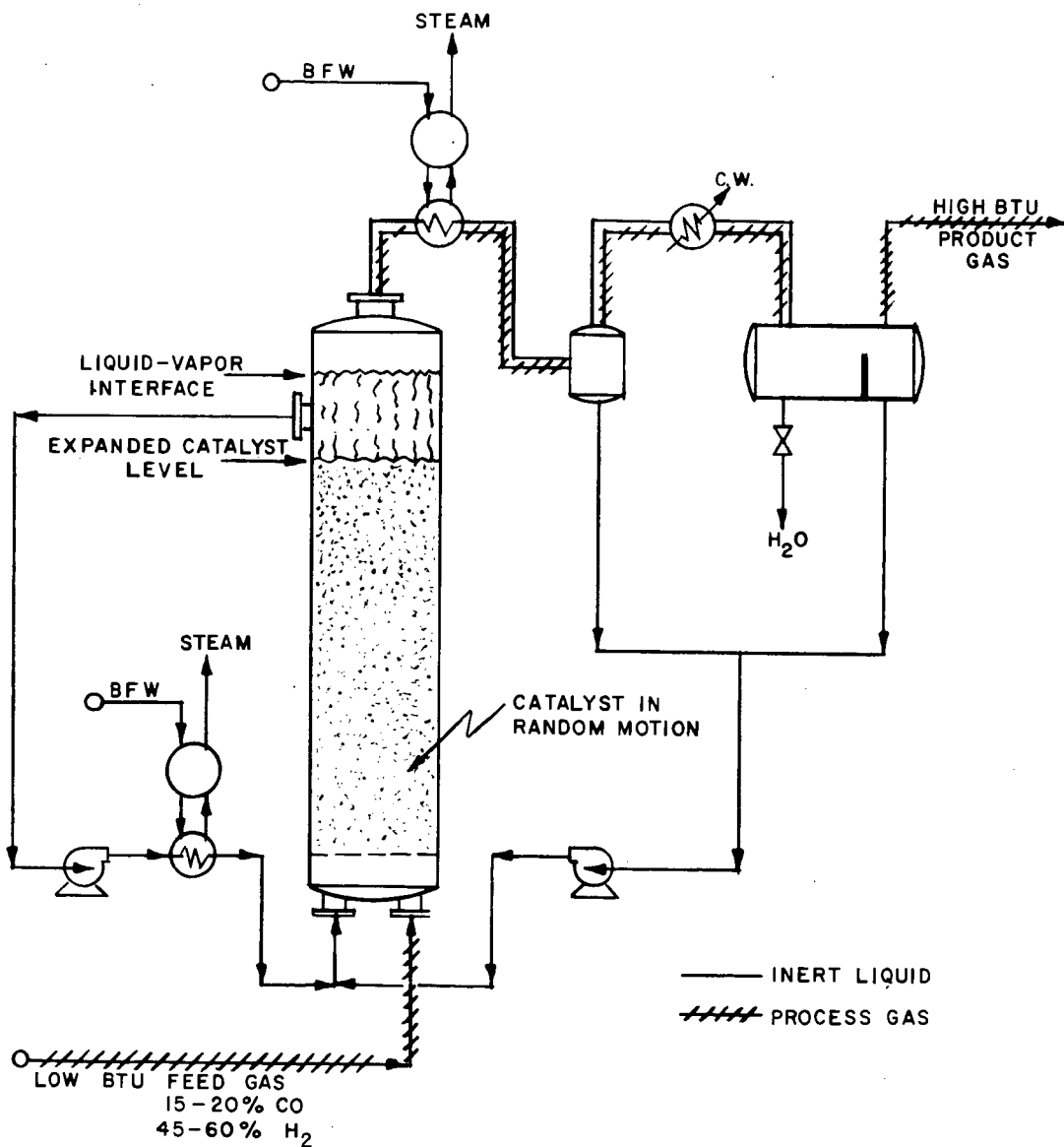


FIGURE 2

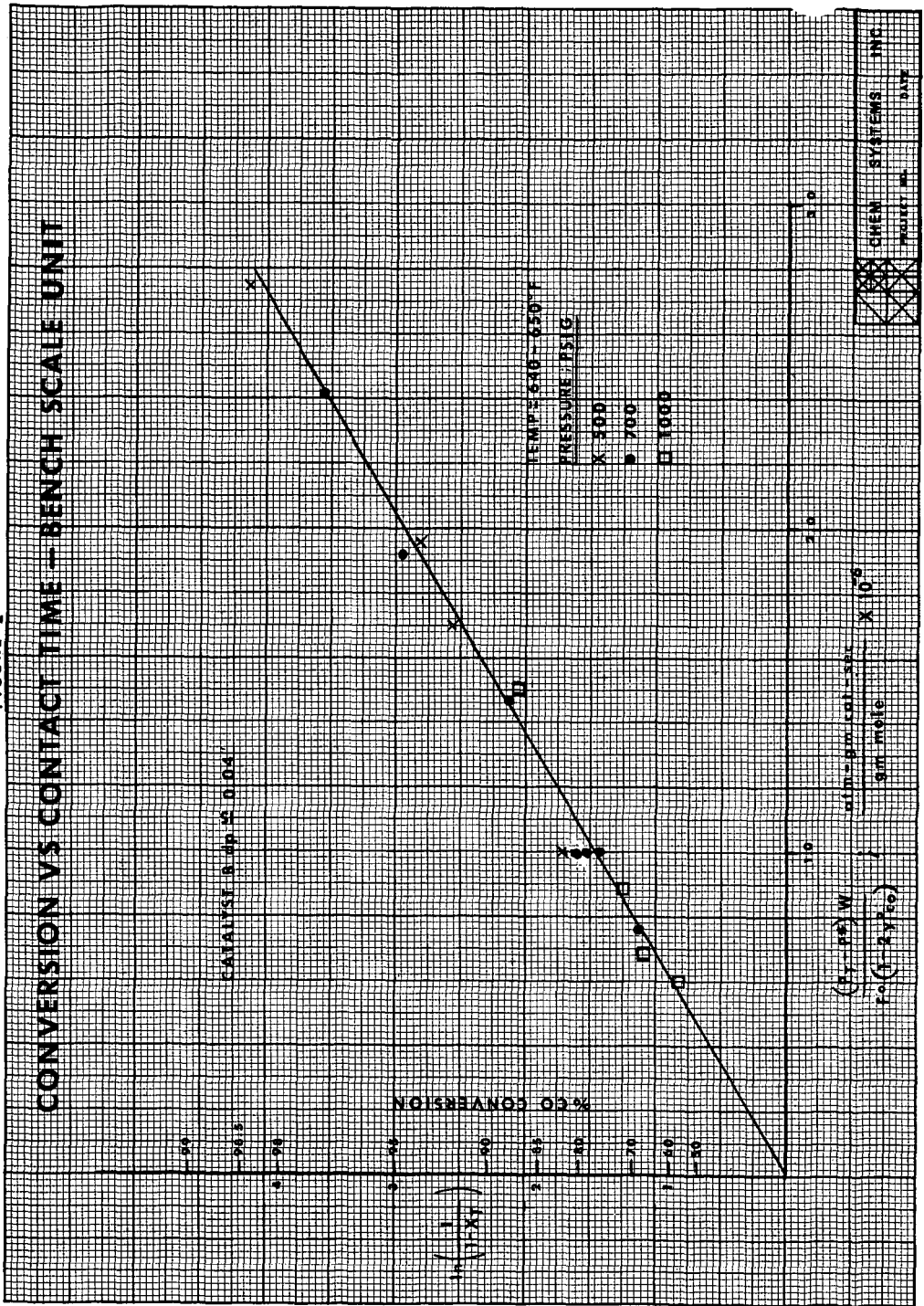


FIGURE 3

TEMPERATURE EFFECT ON KINETIC RATE CONSTANT BENCH SCALE UNIT

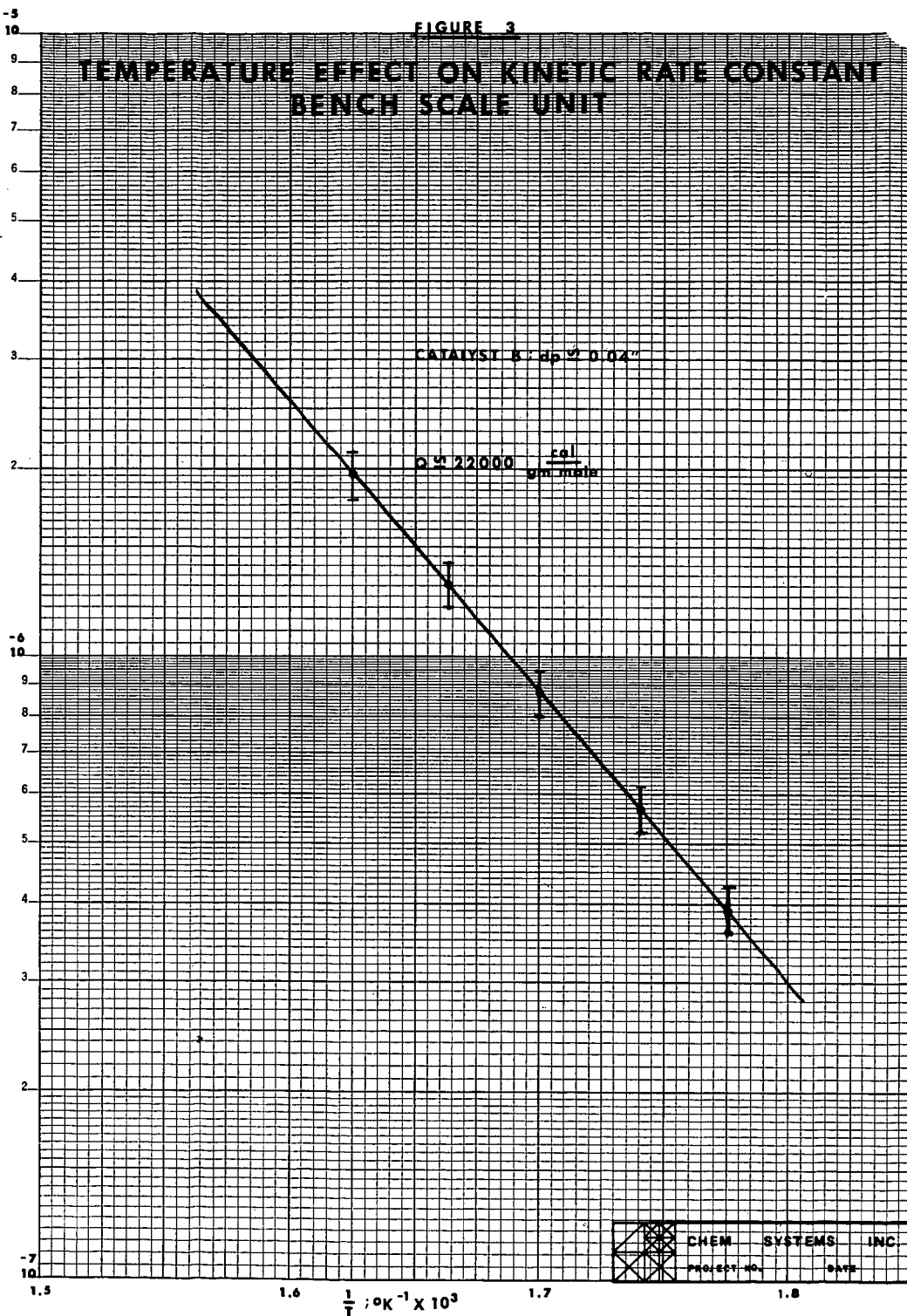
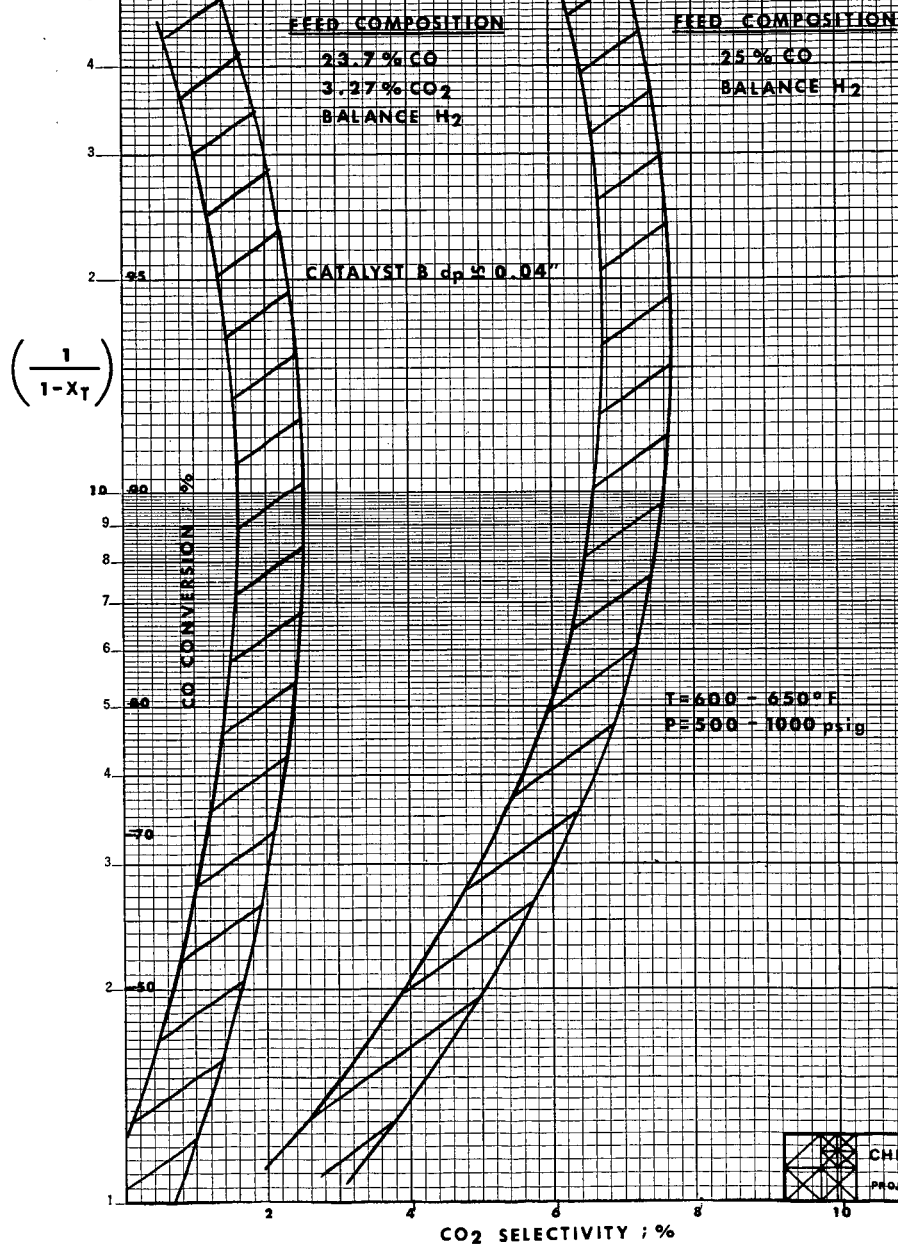
$$\frac{K}{K_H (M/R)} \cdot \frac{\text{gm mole}}{\text{atm-gm cat-sec}}$$


FIGURE 4

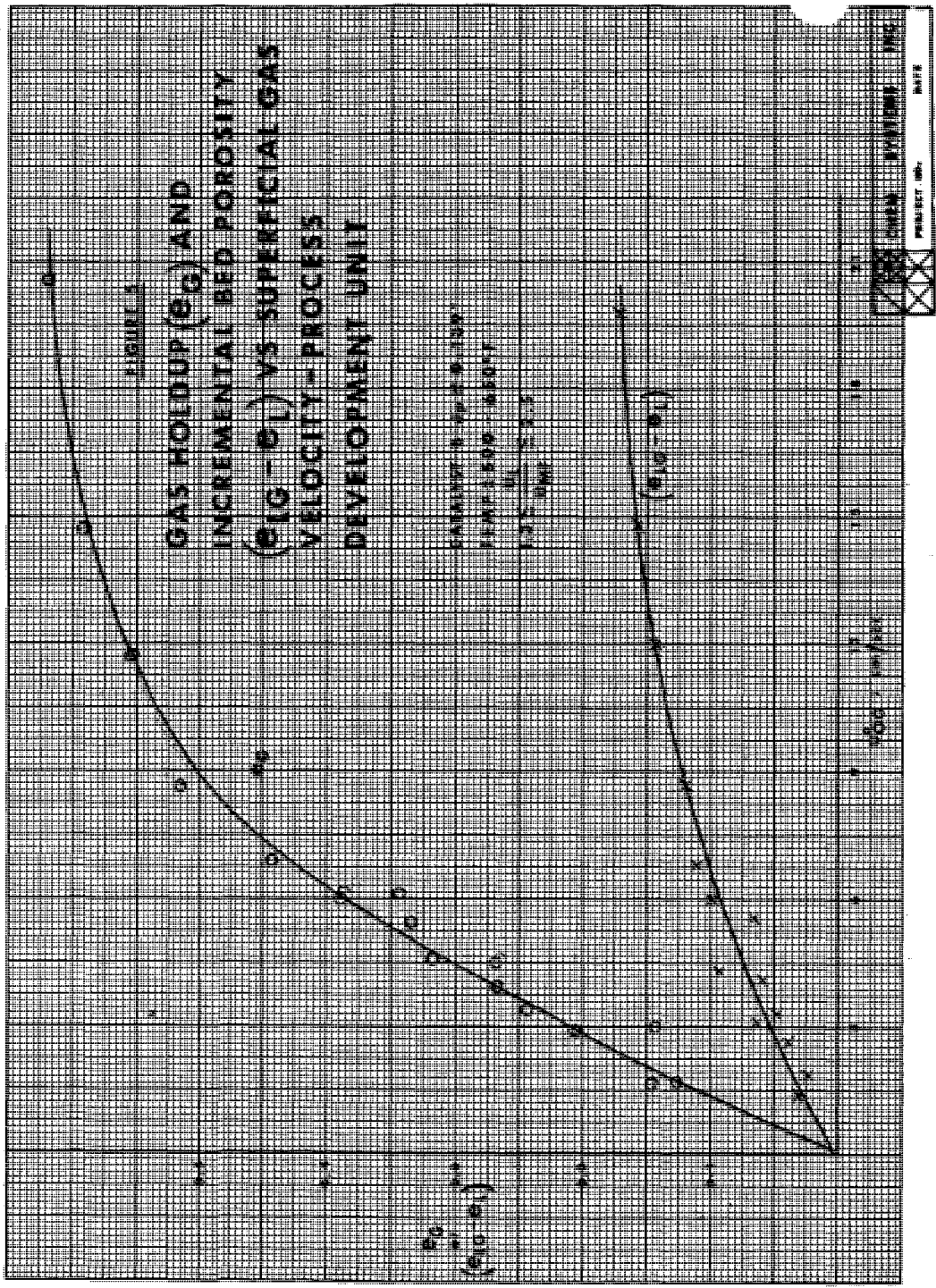
CO₂ SELECTIVITY VS CO CONVERSION



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FIGURE 2
GAS HOLDUP (e_G) AND
INCREMENTAL BED POROSITY
($e_G - e_L$) VS SUPERFICIAL GAS
VELOCITY - PROCESS
DEVELOPMENT UNIT

DATA FROM 4-10-65
REACTOR - 100T
TYPE - 100T
UNIT - 100T



PROJECT NO. _____

DATE _____

DESIGNER _____

CHECKED _____

APPROVED _____

FIGURE 3

CONVERSION VS CONTACT TIME - PROCESS DEVELOPMENT UNIT

CATALYST: R-08200-1307

TEMP: 6.00 ± 0.01 °F

PRESSURE: 100.0

A: 200

B: 300

C: 400

 $\ln\left(\frac{1}{1-x}\right)$

$$\frac{(P_1 - P_2) \times 10^6}{P_1(P_1 - P_2)}$$

$$\frac{(100 - 100) \times 10^6}{100(100 - 100)}$$

$$\frac{0}{0}$$

$$\times 10^6$$

DATE	PROJECT NO.
SYSTEM	

FIGURE 7

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TEMPERATURE EFFECT ON KINETIC RATE CONSTANT PROCESS DEVELOPMENT UNIT

